reflections. Thus, the assignment of crystal class and space group to monoclinic, $P2_1/c$, is correct.

Data collection: Philips PW1100 software. Cell refinement: Philips PW1100 software. Data reduction: Philips PW1100 software. Program(s) used to solve structure: *SAPI91* (Fan, 1991). Program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1985, 1992). Software used to prepare material for publication: *TEXSAN*.

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Formylation *versus* Alkylation of Secondary Amines in DMF

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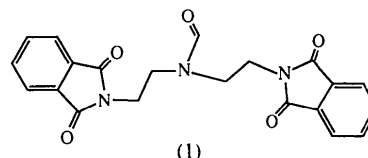
Abstract

2,2'-(Formamidedi-1,2-ethanediyl)bis[1*H*-isoindole-1,3-(2*H*)-dione] (1), $C_{21}H_{17}N_3O_5$, is a product of a slow formylation reaction between refluxing DMF and 2,2'-(iminodi-1,2-ethanediyl)bis[1*H*-isoindole-1,3(2*H*)-dione] (DPDA) which appears to be more efficient than the competing base-promoted alkylation with tris(chloro-

ethyl)amine. The molecules adopt a folded conformation and pack efficiently to form sheets (in the *a* and *c* directions) having a 'W in W' and 'M in M' motif running along the *c* direction.

Comment

Compound (1) was produced as part of a programme of development of synthetic routes to novel, kinetically inert and thermodynamically stable lanthanide polynuclear macrocyclic and dendritic complexes with potential biomedical applications (Matthews, Kahwa & Williams, 1994). Since alkylation of secondary amines in refluxing dimethylformamide (DMF) is readily accomplished using bromoalkyl derivatives and mild base (sodium carbonate or sodium bicarbonate) (Hancock, Cukrowski, Cukrowska, Hosken & Gansow, 1994; Ng, Motekiatis & Martell, 1979), we sought to determine whether significant alkylation yields could be achieved with chloroalkyl starting materials such as tris(chloroethyl)amine (TCEA). However, we find that unlike the bromoalkyls, chloroalkyls appear to be such poor alkylating agents in refluxing DMF that the competing slow formylation reaction (Iwata & Kuzuhara, 1989; Kraus, 1973) dominates. For example, DPDA is readily alkylated in a refluxing sodium carbonate/DMF mixture by α,α'-dibromo-*p*-xylene (Ng, Motekiatis & Martell, 1979) but with TCEA the new compound (1) is a major product. The formation of (1) was determined from elemental, mass and ^1H NMR spectroscopic and X-ray crystallographic analyses.

(1)

The molecular structure and the extended molecular array of (1) are shown in Figs. 1 and 2. The molecule adopts a folded geometry with the phthalimide rings inclined by *ca* 74.7 (1)° with respect to each other. Interatomic distances and angles within the phthalimide residues are normal (Barrett, Kahwa, Mague & McPherson, 1995; Colquhoun, O'Mahoney, Williams, Askari & Mayo, 1994; Barlow, Davidson, Lewis & Russell, 1979). The geometry of the linking N—CH_2—CH_2—N—CH_2—CH_2—N chain is essentially *gauche* with torsion angles about the N—C—C—N bonds in the range 58.6 (3)–79.2 (3)°. Inspection of the geometry of the formamide component of the molecule reveals the expected partial delocalization with a shortening of the N(12)—C(24) bond [1.339 (2) Å] and lengthening of the carbonyl C(24)—O(24) distance [1.218 (2) Å]. There are small out-of-plane deformations within the group, the C(11)—N(12)—C(24)—O(24) and C(13)—N(12)—C(24)—O(24) torsion angles being

1.2 (3) and 176.6 (2)°, respectively. Accompanying these small torsional rotations about the N(12)—C(24) bond there is a slight pyramidalization of the N(12) centre with the N atom lying 0.031 (3) Å out of the plane of its substituents.
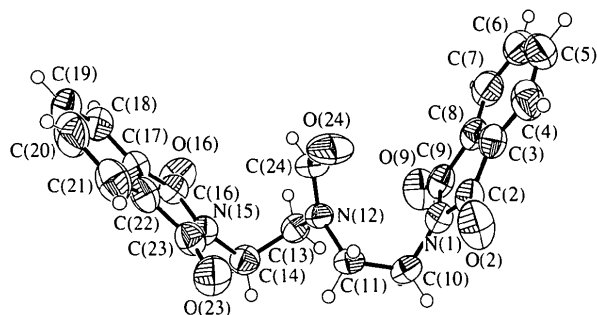

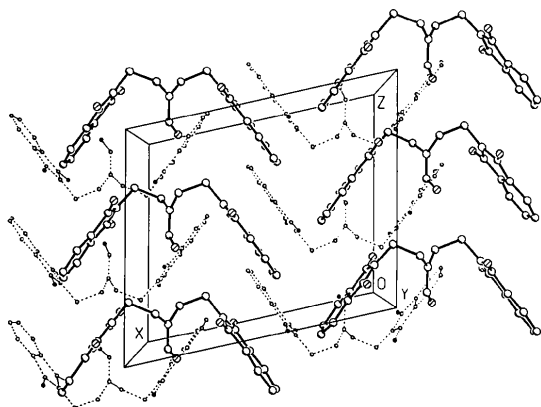Fig. 1. The molecular structure of (1) with 50% probability ellipsoids.

Fig. 2. The extended molecular array of (1) showing the 'W in W' and 'M in M' motif of the layers.

The molecules pack (Fig. 2) to form sheets that extend in the *a* and *c* directions in the crystal. Within each sheet they are arranged in 'W in W'- and 'M in M'-type stacks that run along the *c* direction. One of the *meta* aromatic ring H atoms of the phthalimide unit in one stack is directed towards the face of the aromatic ring of the phthalimide unit of the adjacent stack, and *vice versa*. The distances between the *meta* H atom in one stack and the ring centroid of the phthalimide unit in the next are 2.86 (1) and 2.97 (1) Å. Although within each stack the phthalimide rings are parallel to each other with interplanar separations of 3.5–3.6 Å, there is no π–π overlap.

The shortest intra-stack H—O contact (symmetry operation: x, $\frac{3}{2} - y$, $\frac{1}{2} + z$) is 2.50 (1) Å between the formamide carbonyl O(24) atom in one molecule and one of the methylene H atoms attached to C(10) in another. The O(24)—C(10') distance is 3.19 (1) Å and the associated C—H···O angle is 128 (1)°. The layers of the molecules in the *ac* plane are cross-linked to the adjacent layers in the *b* direction by pairs of weak

C—H···O hydrogen bonds (symmetry operation: $2 - x$, $1 - y$, $-z$) between the *meta* phthalimide C atom C(20) in one sheet and the phthalimide carbonyl O atom O(2) in the next [C(20)—O(2') 3.19 (1), H(20A)—O(2') 2.35 (1) Å, C—H···O 146 (1)°].

Experimental

Diethylenetriamine (100 mmol) and phthalic anhydride (200 mmol) in refluxing acetic acid (160 g) yielded a diphthalimidodiethylaminium–hydrogen phthalate complex (DPDA–HP) (~23 g; 64%) (Barrett, Kahwa, Mague & McPherson, 1995) upon rotavaporation *in vacuo* and recrystallization from ethanol. DPDA–HP and excess potassium carbonate in refluxing acetonitrile gave free DPDA. A mixture of DPDA (110 mmol) and tris(chloroethyl)amine (35 mmol) in DMF was refluxed for a month, cooled and treated with water to selectively yield crude (1) as a beige gummy product (44 mmol; ~40%). The crude product was dissolved in chloroform, dried on magnesium sulfate, and after rotavaporization and subsequent recrystallization from a chloroform/butanol mixture, pure (1) was obtained as light-brown plates. Elemental analyses (MEDAC Ltd, Brunel University, England) of the crude and recrystallized products were similar and consistent with (1): C 64.23, H 4.33, N 10.73%. FAB MS (Kratos Concept 1 H Spectrometer; MNBA matrix): $m/z = 783$ [(1 + 1) + H]$^+$; 393 (1 + H)$^+$; 364 (1 − CO)$^+$; 174 (phthalimidoethyl)$^+$. ^{1}H NMR (CDCl$_3$, 200 MHz, Brucker AC200, δ p.p.m.): 3.62 (triplet), 3.72 (triplet), 3.89 (multiplet), 7.70 (broad multiplet) and 7.85 (multiplet).

Crystal data

$C_{21}H_{17}N_3O_5$	Cu $K\alpha$ radiation
$M_r = 391.4$	$\lambda = 1.54178$ Å
Monoclinic	Cell parameters from 18
$P2_1/c$	reflections
$a = 14.062 (4)$ Å	$\theta = 3.2–16.1°$
$b = 12.046 (2)$ Å	$\mu = 0.815$ mm^{-1}
$c = 11.697 (2)$ Å	$T = 291$ K
$\beta = 102.63 (2)°$	Plate
$V = 1933.4 (7)$ Å^3	$0.43 \times 0.43 \times 0.33$ mm
$Z = 4$	Brown
$D_x = 1.345$ Mg m^{-3}	

Data collection

Siemens *P4/RA* diffractometer	$\theta_{max} = 62°$
ω scans	$h = -16 \rightarrow 15$
Absorption correction:	$k = -13 \rightarrow 7$
none	$l = -13 \rightarrow 11$
3187 measured reflections	2 standard reflections
3034 independent reflections	monitored every 100
2712 observed reflections	reflections
$[F > 4\sigma(F)]$	intensity decay:
$R_{int} = 0.0339$	insignificant

Refinement

Refinement on F	$\Delta\rho_{max} = 0.21$ e Å^{-3}
$R = 0.0464$	$\Delta\rho_{min} = -0.24$ e Å^{-3}

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\AA^2$)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
N(1)	0.6478 (1)	0.7383 (1)	0.1000 (1)	0.054 (1)
C(2)	0.6026 (1)	0.6535 (2)	0.0276 (2)	0.059 (1)
O(2)	0.6110 (1)	0.5565 (1)	0.0522 (2)	0.089 (1)
C(3)	0.5443 (1)	0.7084 (2)	−0.0787 (2)	0.056 (1)
C(4)	0.4861 (2)	0.6645 (2)	−0.1778 (2)	0.076 (1)
C(5)	0.4412 (2)	0.7390 (3)	−0.2637 (2)	0.088 (1)
C(6)	0.4547 (2)	0.8517 (3)	−0.2496 (2)	0.090 (1)
C(7)	0.5118 (2)	0.8950 (2)	−0.1484 (2)	0.075 (1)
C(8)	0.5573 (1)	0.8217 (2)	−0.0641 (2)	0.057 (1)
C(9)	0.6237 (1)	0.8420 (2)	0.0509 (2)	0.060 (1)
O(9)	0.6529 (1)	0.9293 (1)	0.0967 (2)	0.085 (1)
C(10)	0.7179 (1)	0.7198 (2)	0.2098 (2)	0.065 (1)
C(11)	0.8185 (1)	0.6911 (2)	0.1901 (2)	0.054 (1)
N(12)	0.8567 (1)	0.7781 (1)	0.1267 (1)	0.046 (1)
C(13)	0.8991 (1)	0.8765 (1)	0.1895 (2)	0.053 (1)
C(14)	1.0009 (1)	0.8567 (2)	0.2621 (2)	0.060 (1)
N(15)	1.0668 (1)	0.8192 (1)	0.1897 (1)	0.052 (1)
C(16)	1.1127 (1)	0.8903 (1)	0.1250 (2)	0.052 (1)
O(16)	1.1064 (1)	0.9899 (1)	0.1247 (1)	0.078 (1)
C(17)	1.1675 (1)	0.8181 (1)	0.0593 (2)	0.052 (1)
C(18)	1.2244 (2)	0.8465 (2)	−0.0184 (2)	0.070 (1)
C(19)	1.2659 (2)	0.7603 (3)	−0.0687 (2)	0.086 (1)
C(20)	1.2512 (2)	0.6521 (3)	−0.0427 (2)	0.091 (1)
C(21)	1.1938 (2)	0.6227 (2)	0.0355 (2)	0.077 (1)
C(22)	1.1526 (1)	0.7089 (2)	0.0865 (2)	0.057 (1)
C(23)	1.0874 (1)	0.7080 (1)	0.1715 (2)	0.057 (1)
O(23)	1.0569 (1)	0.6305 (1)	0.2176 (2)	0.082 (1)
C(24)	0.8583 (2)	0.7631 (2)	0.0137 (2)	0.058 (1)
O(24)	0.8284 (1)	0.6812 (1)	−0.0441 (1)	0.086 (1)

Table 2. *Geometric parameters ($\AA$, °)*

N(1)—C(2)	1.390 (2)	N(1)—C(9)	1.385 (2)
N(1)—C(10)	1.455 (2)	C(2)—O(2)	1.203 (2)
C(2)—C(3)	1.487 (3)	C(3)—C(4)	1.370 (3)
C(3)—C(8)	1.382 (3)	C(4)—C(5)	1.390 (4)
C(5)—C(6)	1.376 (5)	C(6)—C(7)	1.379 (3)
C(7)—C(8)	1.373 (3)	C(8)—C(9)	1.481 (3)
C(9)—O(9)	1.210 (2)	C(10)—C(11)	1.523 (3)
C(11)—N(12)	1.453 (2)	N(12)—C(13)	1.452 (2)
N(12)—C(24)	1.339 (2)	C(13)—C(14)	1.515 (2)
C(14)—N(15)	1.456 (3)	N(15)—C(16)	1.391 (2)
N(15)—C(23)	1.397 (2)	C(16)—O(16)	1.203 (2)
C(16)—C(17)	1.483 (3)	C(17)—C(18)	1.379 (3)
C(17)—C(22)	1.380 (3)	C(18)—C(19)	1.383 (4)
C(19)—C(20)	1.364 (4)	C(20)—C(21)	1.392 (4)
C(21)—C(22)	1.386 (3)	C(22)—C(23)	1.492 (3)
C(23)—O(23)	1.203 (3)	C(24)—O(24)	1.218 (2)
C(2)—N(1)—C(9)	111.9 (1)	C(2)—N(1)—C(10)	123.8 (2)
C(9)—N(1)—C(10)	124.2 (2)	N(1)—C(2)—O(2)	124.1 (2)
N(1)—C(2)—C(3)	106.1 (1)	O(2)—C(2)—C(3)	129.8 (2)
C(2)—C(3)—C(4)	130.8 (2)	C(2)—C(3)—C(8)	107.6 (1)
C(4)—C(3)—C(8)	121.6 (2)	C(3)—C(4)—C(5)	117.0 (2)
C(4)—C(5)—C(6)	121.4 (2)	C(5)—C(6)—C(7)	121.0 (2)
C(6)—C(7)—C(8)	117.7 (2)	C(3)—C(8)—C(7)	121.2 (2)
C(3)—C(8)—C(9)	108.4 (2)	C(7)—C(8)—C(9)	130.4 (2)
N(1)—C(9)—C(8)	106.1 (1)	N(1)—C(9)—O(9)	124.8 (2)
C(8)—C(9)—O(9)	129.1 (2)	N(1)—C(10)—C(11)	111.9 (2)
C(10)—C(11)—N(12)	111.9 (2)	C(11)—N(12)—C(13)	119.2 (1)
C(11)—N(12)—C(24)	119.6 (1)	C(13)—N(12)—C(24)	121.1 (2)
N(12)—C(13)—C(14)	112.9 (1)	C(13)—C(14)—N(15)	111.5 (1)
C(14)—N(15)—C(16)	123.7 (1)	C(14)—N(15)—C(23)	124.5 (2)
C(16)—N(15)—C(23)	111.7 (2)	N(15)—C(16)—O(16)	125.0 (2)
N(15)—C(16)—C(17)	106.1 (1)	O(16)—C(16)—C(17)	128.9 (2)
C(16)—C(17)—C(18)	129.7 (2)	C(16)—C(17)—C(22)	108.5 (2)
C(18)—C(17)—C(22)	121.8 (2)	C(17)—C(18)—C(19)	117.0 (2)
C(18)—C(19)—C(20)	121.5 (3)	C(19)—C(20)—C(21)	121.9 (3)
C(20)—C(21)—C(22)	116.7 (2)	C(17)—C(22)—C(21)	121.0 (2)
C(17)—C(22)—C(23)	107.9 (2)	C(21)—C(22)—C(23)	131.1 (2)
N(15)—C(23)—C(22)	105.8 (2)	N(15)—C(23)—O(23)	124.7 (2)
C(22)—C(23)—O(23)	129.4 (2)	N(12)—C(24)—O(24)	125.5 (2)

The structure was solved by direct methods and the non-H atoms refined anisotropically. All H-atom positions were located in a ΔF map. Their positions were idealized; they were assigned isotropic thermal parameters $U(\text{H}) = 1.2U_{eq}(\text{C})$ and allowed to ride on their parent C atoms. *SHELXTL/PC* (Sheldrick, 1991) was used for all calculations.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1124). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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